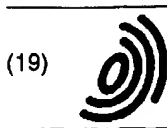


319



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 1 217 616 A2**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
26.06.2002 Bulletin 2002/26

(51) Int Cl.7: **G11B 5/712**

(21) Application number: **02003195.1**

(22) Date of filing: **17.11.1997**

(84) Designated Contracting States:
AT BE CH DE DK ES FI FR GB GR IE IT LI NL PT SE

• **Tyler, Malvin Nicolas**
Bath BA1 2EW (GB)

(30) Priority: **16.11.1996 GB 9623851**

(74) Representative: **Nash, David Allan**
Haseltine Lake & Co.,
Imperial House, 15-19 Kingsway
London WC2B 6UD (GB)

(62) Document number(s) of the earlier application(s) in
accordance with Art. 76 EPC:
97912368.4 / 0 938 728

Remarks:

This application was filed on 18 - 02 - 2002 as a
divisional application to the application mentioned
under INID code 62.

(71) Applicant: **Nanomagnetics Limited**
Bristol, BS16 7FG (GB)

(72) Inventors:
• **Mayes, Eric Leigh**
Bath BA1 26N (GB)

(54) **Magnetic composition**

(57) According to the invention, there is provided a
composition comprising a plurality of uniformly sized fer-
romagnetic metal alloy or metal ferrite particles, each of
which is encased or partially encased within an organic

macromolecule, and each of which has a largest dimen-
sion no greater than 100nm.

EP 1 217 616 A2

Description

MAGNETIC COMPOSITION

[0001] This invention relates to a magnetizable device which comprises a magnetic layer composed of domain-separated, nanoscale (e.g. 1-100nm) ferromagnetic particles. The magnetizable device of the invention may be used as a magnetic storage device having improved data storage characteristics. In particular, the invention relates to magnetic storage media comprising single-domain, domain-separated, uniform, ferromagnetic nanoscale (e.g. 1-100 nm) particles which may be arranged into a regular 2-D packed array useful in the storage of information.

[0002] Among the possible pathways to ultrahigh-density (>1 Gbit/in²) magnetic media is the use of nanoscale (1-100 nm) particles. Beyond the standard requirements for magnetic media, a viable particulate media should have a small standard deviation in particle size as well as the particles being exchange decoupled. These requirements are necessary to avoid adverse media noise. Current methods of fabricating nanoscale particles, such as arc-discharge or multiple target ion-beam sputtering, have not fully addressed these two requirements. Moreover, if the uniform particles are arranged into an ordered array, each particle can represent a "bit" of information at a predictable location further increasing the media's efficiency. This invention details methods of producing particulate media that meet these requirements for ultrahigh-density recording. This invention is also an open system which allows for the production of a variety of magnetic materials, such that the media can be tuned for different applications.

[0003] In particular this invention details the use of an iron storage protein, ferritin, whose internal cavity is used to produce the nanoscale particles. Ferritin is utilised in iron metabolism throughout living species and its structure is highly conserved among them. It consists of 24 subunits which are arranged to provide a hollow shell roughly 8 nm in diameter. The cavity normally stores 4500 iron(III) atoms in the form of paramagnetic ferrihydrite. However, this ferrihydrite can be removed (a ferritin devoid of ferrihydrite is termed "apoferritin") and other materials may be incorporated. Examples include ceramics, superparamagnetic magnetite, acetaminophen, and even the sweetener aspartame. To address magnetic media concerns, the invention incorporates ferromagnetically ordered materials.

[0004] According to a first aspect of the present invention, there is provided a magnetizable device which comprises a magnetic layer composed of domain-separated, ferromagnetic particles each of which has a largest dimension no greater than 100nm.

[0005] According to a second aspect of the invention, there is provided a magnetic recording medium which includes a magnetizable layer, wherein said magnetizable layer comprises a plurality of ferromagnetic parti-

cles each having a largest dimension no greater than 100nm, and each of which particles represents a separate ferromagnetic domain. The magnetizable layer is preferably supported on a nonmagnetic substrate.

[0006] According to a third aspect of the present invention, there is provided a magnetic composition comprising a plurality of ferromagnetic particles each of which is bound to an organic macromolecule, and each of which has a largest dimension no greater than 100nm. In this aspect of the invention, it is preferred that said organic macromolecule is ferritin from which the normal core ferrihydrite has been removed and replaced by a ferromagnetic particle.

[0007] As used herein, the term "ferromagnetic" embraces materials which are either "ferromagnetic" and "ferrimagnetic". Such usage is common in the electrical engineering art.

[0008] The ferromagnetic particles used in the invention should be of a material and size such that they possess ferromagnetic properties at ambient temperatures (e.g. 15°C to 30°C).

[0009] Preferably, the ferromagnetic particles each have a largest dimension no greater than 50nm, more preferably less than 25nm and most preferably smaller than 15nm. The largest dimension of the ferromagnetic particles should not be so small that the particle will lose its ferromagnetic property and become superparamagnetic at the desired operating temperature of the recording medium. Typically, for operation at ambient temperature, this means that the magnetic particles will normally be no smaller than about 3nm in their largest diameter.

[0010] In the magnetizable device of the first aspect of this invention and the magnetic recording medium of the second aspect of this invention, the distance between adjacent ferromagnetic domains is preferably as small as possible to permit the maximum number of discrete domains in a given area, and provide the maximum storage capacity for the recording medium. The actual lower limit will vary for different materials and other conditions such as the temperature at which the recording medium is to be used. The key requirement, however, is that neighbouring domains should not be able to interfere magnetically with each other to the extent that the magnetic alignment of any domain can be altered by neighbouring domains. Typically, the lower limit on the spacing of the domains is about 2nm. The distance between adjacent domains will be determined by the density of discrete domains required. Typically, however, to take advantage of the miniaturization possibilities provided by the invention, the distance between adjacent domains will be no greater than 10nm.

[0011] Generally the particles will be uniform in size, by which we mean that the particles do not vary in largest diameter by more than about 5%. One of the advantages of the use in the invention of an organic macromolecule which binds a magnetic particle by surrounding it is that this can be used to select particles of a uni-

form size.

[0012] In the case where the particles are spheroidal, it will be the diameter of the particles which must be no greater than 100nm.

[0013] In preferred embodiments of all aspects of this invention, each ferromagnetic particle is encased, or partially encased, within an organic macromolecule. The term macromolecule means a molecule, or assembly of molecules, and may have a molecular weight of up to 1500kD, typically less than 500kD. Ferritin has a molecular weight of 400kD.

[0014] The macromolecule should be capable of binding by encasing or otherwise organising the magnetic particle, and may therefore comprise a suitable cavity capable of containing the particle; a cavity will normally be fully enclosed within the macromolecule. Alternatively, the macromolecule may include a suitable opening which is not fully surrounded, but which nevertheless is capable of receiving and supporting the magnetic particle; for example, the opening may be that defined by an annulus in the macromolecule. For example, suitable macromolecules which may be used in the invention are proteins, for example the protein apoferritin (which is ferritin in which the cavity is empty), flagellar L-P rings, cyclodextrins, self-assembled cyclic peptides. As an alternative to encasing the magnetic particles within the macromolecule, they may be organised on the macromolecule, such as on a bacterial S-layer.

[0015] Other materials which may be used in the invention to organise the ferromagnetic particles are inorganic-silica networks such as MCM type materials, dendrimers and micellar type systems.

[0016] The presently preferred macromolecule for use in the invention is the apoferritin protein which has a cavity of the order of 8nm in diameter. The ferri- or ferromagnetic particles to be accommodated within this protein should have a diameter no greater than 8nm.

[0017] The bound particles of this aspect of the present invention with a coating that inhibits aggregation and oxidation, also helping them to be domain-separated.

[0018] In the magnetizable device of the first aspect of this invention and the magnetic recording medium of the second aspect of this invention, the particles are preferably arranged in a 2-D ordered array which would yield an ultrahigh-density magnetic media.

[0019] The ferromagnetic material may be a metal, such as cobalt, iron, or nickel; a metal alloy, such as an alloy which contains aluminium, barium, bismuth, cerium, chromium, cobalt, copper, iron, manganese, molybdenum, neodymium, nickel, niobium, platinum, praseodymium, samarium, strontium, titanium, vanadium, yttrium, or a mixture thereof; a metal ferrite such as a ferrite containing barium, cobalt, or strontium; or an organic ferromagnetic material.

[0020] When generating nanoscale particles, one major concern is that the particles produced are not superparamagnetic. Superparamagnetic particles are those

which have permanent magnetic dipole moments, but the moments' orientations with respect to the crystallographic axes fluctuate with time. This is not useful for a practical magnetic storage media. Superparamagnetism depends on the volume, temperature, and anisotropy of the particles. Via energy considerations, one can derive an equation relating these quantities. The volume at which a particle becomes superparamagnetic (V_p) is given by: $V_p = 25kT/K$, where k is Boltzmann's constant, T the temperature of the particle in degrees Kelvin, and K the anisotropy constant of the material. Using this formula, it is possible to determine the temperature at which a particle becomes superparamagnetic (the "blocking temperature") for a given material at a fixed volume. In our specific case, the fixed volume is 8 nm in ferritin. If a cobalt metal particle with only crystalline anisotropy (that value being 45×10^5) is a sphere with a diameter of 8 nm, the blocking temperature is 353°K. This is within the range of temperatures experienced within a hard disk drive, and the cobalt particles may prove to be a useful storage medium. Obviously, there are other considerations such as the materials' coercivity, moment, saturation magnetisation, and relaxation time. By tuning the materials incorporated into the ferritin, though, these can be addressed.

[0021] Ferritin is utilised in iron metabolism throughout living species and its structure is highly conserved among them. It consists of 24 subunits arranged in a 432 symmetry which provide a hollow shell roughly 8 nm in diameter. The cavity normally stores 4500 iron(III) atoms in the form of paramagnetic ferrihydrite. However, this ferrihydrite can be removed (a ferritin devoid of ferrihydrite is termed "apoferritin") and other materials may be incorporated. The subunits in ferritin pack tightly, however there are channels into the cavity at the 3-fold and 4-fold axes. Lining the 3-fold channels are residues which bind metals such as cadmium, zinc, and calcium. By introducing such divalent ions one can potentially bind ferritin molecules together, or at least encourage their proximal arrangement.

[0022] One method of preparing a 2-D packed array of ferromagnetically ordered particles of uniform size up to 8 nm includes the removal of the ferrihydrite core from the native ferritin in aqueous solution, the incorporation of ferromagnetically ordered cobalt metal particles by sodium borohydride reduction of the aqueous Co(II) solution into the ferritin cavities, the generation of a narrow size distribution through ultracentrifugation, the injection of particles into an MES/glucose subphase solution upon which the 2-D array assembles, and the transfer of the 2-D array to a substrate which is then carbon coated. In this method, the ferritin source may be a vertebrate, invertebrate, plant, fungi, yeast, bacteria, or one produced through recombinant techniques.

[0023] In the method described, a metal alloy core may be produced by sodium borohydride reduction of a water soluble metal salt. Other oxidation methods include carbon, carbon monoxide, hydrogen, or hydrazine

hydrate solution. Alternatively, a suitable solution may be oxidised to yield a metal ferrite core. Oxidation may be chemical or electrochemical to yield the metal ferrite. [0024] In this method, other methods of selecting a narrow size distribution may be employed such as short or long column meniscus depletion methods or magnetic field separation.

[0025] Further, in this method, divalent metal salts containing cadmium, calcium, or zinc may be added into the subphase solution to aid in particle ordering.

[0026] Further, in this, other methods of arranging the particles into a 2-D array may be employed, such as solution evaporation onto a solid substrate.

[0027] Further, in this method, the 2-D array may be coated with carbon-based films such as hydrogenated or nitrogen doped diamond-like carbon, or with silicon-based films such as silicon dioxide.

[0028] In the present invention, ferritin may be used to enclose a ferromagnetic particle whose largest dimension is limited by ferritin's inner diameter of 8 nm. The particles are produced first by removing the ferrihydrite core to yield apoferritin. This is done by dialysis against a buffered sodium acetate solution under a nitrogen flow. Reductive chelation using thioglycolic acid is used to remove the ferrihydrite core. This is followed by repeated dialysis against a sodium chloride solution to completely remove the reduced ferrihydrite core from solution. Once the apoferritin is produced, ferri- or ferromagnetic particles are incorporated in the following ways. The first is by reducing a metal salt solution in the presence of apoferritin. This is performed in an inert atmosphere to protect the metal particles from oxidation which would lessen their magnetic benefit. A combination of metal salts in solution can also be reduced to generate alloys or alloy precursors. Sintering or annealing in a magnetic field may be necessary to generate the useful magnetic alloys. Another method is to oxidise a combination of an iron(II) salt and another metal salt. This gives a metal ferrite particle which does not suffer negatively from oxidation. The metal salts which are beneficial include salts of aluminium, barium, bismuth, cerium, chromium, cobalt, copper, iron, manganese, molybdenum, neodymium, nickel, niobium, platinum, praseodymium, samarium, strontium, titanium, vanadium, ytterbium, and yttrium.

[0029] A narrow size distribution of particles is necessary to avoid media noise. Such a distribution can be obtained through a variety of procedures including, but not limited to, density gradient centrifugation or magnetic field separation.

[0030] While the production procedure detailed uses native horse spleen ferritin, this invention should not be seen as limited to that source. Ferritin can be found in vertebrates, invertebrates, plants, fungi, yeasts, bacteria, or even produced through recombinant techniques. By creating mutant apoferritins lacking the divalent binding site, others have found that the mutant proteins assemble into oblique assemblies as opposed to the reg-

ular hexagonal close-packed.

[0031] While ferritin seems to be an ideal system for generating nanoscale particles, it is not the only system available. For example, flagellar L-P rings are tubular proteins with an inner diameter of 13 nm. By creating a 2-D array of these proteins, metal films could be deposited into the tubular centres to create perpendicular rods of magnetic material. Also metal reduction in the presence of a microemulsion can be used to generate nanoscale particles which are coated with surfactant. This invention is open to other nanoscale particle production methods.

[0032] Finally an ordered arrangement of the particles is desired. One way to accomplish this is by injecting an aqueous solution of particles into an MES/glucose subphase solution contained in a Teflon trough. The particles spread at the air-subphase interface, and a portion denature to form a monolayer film. The 2-D arrangement of encased particles occurs underneath this monolayer. After 10 minutes at room temperature, the arrangement and monolayer are transferred to a substrate by placing the substrate directly onto the monolayer for 5 minutes. After withdrawing the substrate, the attached arrangement is coated with a thin layer of carbon for protection. Other methods such as solution evaporation onto a solid substrate can also give 2-D arrangements, and this invention should not be seen as limited in its arrangement methods.

EXAMPLE 1

[0033] This example illustrates the preparation of apoferritin from horse spleen ferritin. Apoferritin was prepared from cadmium-free native horse spleen ferritin (CalBiochem, 100 mg/ml) by dialysis (molecular weight cut-off of 10-14 kDaltons) against sodium acetate solution (0.2 M) buffered at pH 5.5 under a nitrogen flow with reductive chelation using thioglycolic acid (0.3 M) to remove the ferrihydrite core. This is followed by repeated dialysis against sodium chloride solution (0.15 M) to completely remove the reduced ferrihydrite core from solution.

EXAMPLE 2

[0034] This example illustrates the preparation of cobalt metal within apoferritin. The apoprotein is added to a deaerated TES/sodium chloride solution (0.1/0.4 M) buffered at pH 7.5 to give an approximate 1 mg/ml working solution of the protein. A deaerated cobalt(II) [for example, as the acetate salt] solution (1 mg/ml) was added incrementally such that the total number of atoms added was approximately 500 atoms/apoprotein molecule. This was allowed to stir at room temperature for one day in an inert atmosphere. This is followed by reduction of the cobalt(II) salt with sodium borohydride to cobalt(0) metal. The final product yielded a solution of cobalt particles, each surrounded by a ferritin shell.

EXAMPLE 3

[0035] This example illustrates the preparation of a metal alloy such as yttrium cobalt (YCo5) within apoferritin. The metal alloy follows the same procedure as Example 2 but using a 1:5 ratio of yttrium(III) [for example, as the acetate salt] to cobalt(II) [for example, as the acetate salt]. The final product yielded a solution of yttrium cobalt particles, each surrounded by a ferritin shell.

EXAMPLE 4

[0036] This example illustrates the preparation of a metal ferrite such as cobalt ferrite (CoO.Fe2O3) within apoferritin. The apoprotein is added to a deaerated MES/sodium chloride solution (0.1/0.4 M) buffered at pH 6 to give an approximate 1 mg/ml working solution of the protein. A deaerated solution of cobalt(II) [for example, as the acetate salt] and iron(II) [for example, as the ammonium sulphate salt] in a ratio of 1:2 is added incrementally and allowed to air-oxidise. The final product yielded a solution of cobalt ferrite particles, each surrounded by a ferritin shell.

EXAMPLE 5

[0037] This example illustrates the 2-D arrangement of ferritin-encased magnetic particles. An aqueous solution of particles [from Examples 2-4, and whose uniformity in size has been selected] is injected into an MES/glucose subphase solution (0.01 M/2%) contained in a Teflon trough. The particles spread at the air-subphase interface, and a portion denature to form a monolayer film. The 2-D arrangement of encased particles occurs underneath this monolayer. After 10 minutes at room temperature, the arrangement and monolayer are transferred to a substrate by placing the substrate directly onto the monolayer for 5 minutes. After withdrawing the substrate, the attached arrangement is coated with a thin layer of carbon for protection.

Claims

1. A composition comprising a plurality of uniformly sized ferromagnetic metal alloy or metal ferrite particles, each of which is encased or partially encased within an organic macromolecule, and each of which has a largest dimension no greater than 100nm.
2. A composition according to claim 1, wherein the ferromagnetic particles do not differ by more than 5% in their largest dimension.
3. A composition according to claim 1 or 2, wherein the organic macromolecule comprises a protein.
4. A composition according to claim 3, wherein the organic macromolecule is apoferritin.
5. A composition according to any preceding claim, wherein the particles are spheroidal.
6. A composition according to any preceding claim, wherein the particles are metal alloy particles in which the alloy contains aluminium, barium, bismuth, cerium, chromium, cobalt, copper, iron, manganese, molybdenum, neodymium, nickel, niobium, platinum, praseodymium, samarium, strontium, titanium, vanadium, ytterbium, yttrium or mixtures thereof.
7. A composition according to any one of claims 1 to 5, wherein the particles are metal ferrite particles, wherein the ferrite contains barium, cobalt or strontium.
8. A composition comprising a plurality of uniformly sized ferromagnetic metal alloy or metal ferrite particles each formed within the cavity of an apoferritin protein macromolecule.
9. A process for preparing uniformly sized ferromagnetic metal alloy or metal ferrite particles each of which has a largest dimension no greater than 100nm, which process comprises the step of forming said particles within an organic macromolecule.
10. A process according to claim 9, wherein the ferromagnetic particles do not differ by more than 5% in their largest dimension.
11. A process according to claim 9 or 10, wherein the particles are spheroidal.
12. A process according to claim 9, 10 or 11, wherein the organic macromolecule is a protein.
13. A process according to claim 12, wherein the organic macromolecule is apoferritin.
14. A process according to claim 12, wherein the particles are metal alloy particles which are formed by reducing a combination of metal salts in solution in the presence of apoferritin.
15. A process according to claim 14, wherein the metal alloy particles are annealed in a magnetic field.
16. A process according to claim 12, wherein the particles are metal ferrite particles which are formed by oxidising a combination of an iron (II) salt and another metal salt.
17. A process for preparing nanoscale metal particles

in which the metal particles are formed by reduction
in the presence of a microemulsion.

18. A process according to claim 17, wherein the particles are metal alloy particles which are formed by reducing a combination of metal salts in solution in the presence of the microemulsion. 5

19. A process according to claim 18, wherein the metal alloy particles are annealed in a magnetic field. 10

15

20

25

30

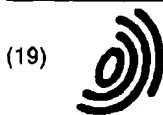
35

40

45

50

55



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 1 217 616 A3**

(12) **EUROPEAN PATENT APPLICATION**

(88) Date of publication A3:
11.09.2002 Bulletin 2002/37

(51) Int Cl.7: **G11B 5/712, H01F 1/00**

(43) Date of publication A2:
26.06.2002 Bulletin 2002/26

(21) Application number: **02003195.1**

(22) Date of filing: **17.11.1997**

(84) Designated Contracting States:
**AT BE CH DE DK ES FI FR GB GR IE IT LI NL PT
SE**

(30) Priority: **16.11.1996 GB 9623851**

(62) Document number(s) of the earlier application(s) in
accordance with Art. 76 EPC:
97912368.4 / 0 938 728

(71) Applicant: **Nanomagnetics Limited**
Bristol, BS16 7FG (GB)

(72) Inventors:

- **Mayes, Eric Leigh**
Bath BA1 26N (GB)
- **Tyler, Malvin Nicolas**
Bath BA1 2EW (GB)

(74) Representative: **Nash, David Allan**
Haseltine Lake & Co.,
Imperial House, 15-19 Kingsway
London WC2B 6UD (GB)

(54) **Magnetic composition**

(57) According to the invention, there is provided a composition comprising a plurality of uniformly sized ferromagnetic metal alloy or metal ferrite particles, each of which is encased or partially encased within an organic

macromolecule, and each of which has a largest dimension no greater than 100nm.

EP 1 217 616 A3

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 02 00 3195

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	US 5 491 219 A (MANN) 13 February 1996 (1996-02-13)	1-5, 7-13, 16	G11B5/712 H01F1/00
Y	* column 2, line 12 - line 16 * * column 2, line 33 - line 48 * * column 4, line 6 - line 18; claims 1, 6 *	6, 14, 15	
X	US 5 062 991 A (SIIMAN ET AL.) 5 November 1991 (1991-11-05)	1-3, 5, 7, 9-12, 16	
	* column 3, line 20 - line 30 * * column 6, line 4 - line 6; claims 1, 11 *		
X	US 5 147 841 A (WILCOXON) 15 September 1992 (1992-09-15)	17, 18	
Y	* column 3, line 1 - line 40 * * column 4, line 15 - line 41 * * column 5, line 32 - line 34 * * column 11, line 35 *	14, 15, 19	
X	US 4 425 261 A (STENIUS ET AL.) 10 January 1984 (1984-01-10)	17	
	* claims 1, 3, 6 *		
X	DE 42 44 354 A (HIRAI) 1 July 1993 (1993-07-01)	17	G11B H01F
	* column 2, line 17 - line 35 * * column 6, line 24 - line 26 *		
X	EP 0 686 448 A (AUSIMONT) 13 December 1995 (1995-12-13)	17	
	* page 2, line 46 - line 54; claim 1 *		
Y	EP 0 049 770 A (ALLIED) 21 April 1982 (1982-04-21)	15, 19	
	* claims 1, 2, 7 *		
-/-			
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 19 July 2002	Examiner Magrizos, S
CATEGORY OF CITED DOCUMENTS		T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date O: document cited in the application I: document cited for other reasons A: member of the same patent family, corresponding document X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document	

EPO FORM P/0101/01 (Rev. 01/01)



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 02 00 3195

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
Y	US 4 009 111 A (TAMAI ET AL.) 22 February 1977 (1977-02-22) * column 6, line 10 - line 36 * * column 6, line 65 - line 67 * * column 7, line 29 - line 32 * * column 9, line 24 - line 29 * -----	14	
Y	US 5 574 961 A (EDELSTEIN ET AL.) 12 November 1996 (1996-11-12) * column 4, line 58 - line 64; claim 1 * -----	6	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
Place of search		Date of completion of the search	Examiner
THE HAGUE		19 July 2002	Magrizos, S
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document</p> <p>T: theory or principle underlying the invention B: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons S: member of the same patent family, corresponding document</p>			

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 02 00 3195

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

19-07-2002

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5491219	A	13-02-1996	NONE	
US 5062991	A	05-11-1991	AT 126384 T AU 654285 B2 AU 8183791 A CA 2084414 A1 DE 69112057 D1 DE 69112057 T2 EP 0532684 A1 ES 2077235 T3 JP 5509203 T WO 9119301 A1 US 5240640 A	15-08-1995 03-11-1994 31-12-1991 05-12-1991 14-09-1995 11-01-1996 24-03-1993 16-11-1995 16-12-1993 12-12-1991 31-08-1993
US 5147841	A	15-09-1992	NONE	
US 4425261	A	10-01-1984	DE 3161354 D1 DK 514181 A ,B, EP 0055257 A1 FI 821138 A ,B, JP 2051666 B JP 57500324 T NO 813957 A ,B, WO 8102688 A1	15-12-1983 19-11-1981 07-07-1982 01-04-1982 08-11-1990 25-02-1982 20-11-1981 01-10-1981
DE 4244354	A	01-07-1993	DE 4244354 A1 JP 3209816 B2 JP 5271718 A US 6051614 A	01-07-1993 17-09-2001 19-10-1993 18-04-2000
EP 686448	A	13-12-1995	IT 1279200 B AT 179916 T DE 69509586 D1 DE 69509586 T2 EP 0686448 A2 ES 2132460 T3 JP 8038880 A US 5725802 A	29-04-1997 15-05-1999 17-06-1999 23-09-1999 13-12-1995 16-08-1999 13-02-1996 10-03-1998
EP 49770	A	21-04-1982	US 4409041 A AT 21417 T AU 551753 B2 AU 7555481 A CA 1181262 A1 DE 3175108 D1 EP 0049770 A2	11-10-1983 15-08-1986 08-05-1986 01-04-1982 22-01-1985 18-09-1986 21-04-1982

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.

EP 02 00 3195

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on the European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

19-07-2002

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 49770	A		ES 505808 D0	01-09-1982
			ES 8206642 A1	16-11-1982
			JP 1295038 C	26-12-1985
			JP 57094554 A	12-06-1982
			JP 60017019 B	30-04-1985
			US 4889568 A	26-12-1989
US 4009111	A	22-02-1977	JP 1089908 C	23-03-1982
			JP 50041506 A	16-04-1975
			JP 56033775 B	06-08-1981
			CA 1035208 A1	25-07-1978
			US 3943012 A	09-03-1976
US 5574961	A	12-11-1996	NONE	

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82